

## 2-PHENYL-6-BENZOTHAZOLYL ISOTHIOCYANATES

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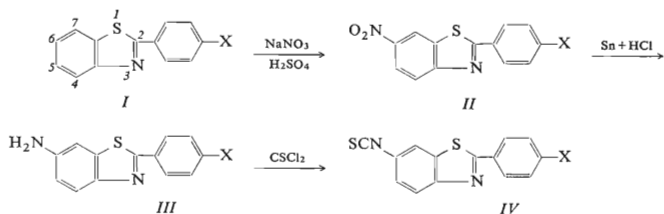
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Synthesis of substituted 2-phenyl-6-benzothiazolyl isothiocyanates and their intermediate products, especially the possibility of direct nitration of benzothiazole ring, is described. The IR and UV spectra of the isothiocyanates were measured and kinetics of their reactions with  $\text{OH}^-$  ions and with  $\text{NH}_2$  group of glycine were studied. Contrary to 2-phenyl-5-benzothiazolyl isothiocyanates, for which substituent effects were found to be negligible, in the case of 2-phenyl-6-benzothiazolyl isothiocyanates, the rate constants of studied reactions were found to correlate well with  $\sigma$  substituent constants.

Benzothiazole derivatives exhibit wide biological activity, *e.g.* as tuberculostatics<sup>1,2</sup>, antihelmintics<sup>3</sup>, fungicides<sup>4</sup>, and as compounds enhancing the activity of some analgetics<sup>5</sup>; these derivatives affect also fermentation processes<sup>6</sup>. In continuing our previous studies<sup>7</sup> we were concerned with the effect of substituents in the 4' position of 2-phenyl ring on the properties of the NCS group attached to the 6 position of benzothiazole skeleton. We have recently reported<sup>8,9</sup> that reactivity of the NCS group in the 5 position of benzothiazole ring is little sensitive to substituent effects.

Derivatives of 2-phenyl-6-benzothiazolyl isothiocyanates were synthesized according to Scheme 1. Benzothiazole skeleton was prepared by condensation of zinc salt of 2-aminothiophenol with substituted benzoyl chlorides<sup>10,11</sup>. The reaction course was found to strongly depend on the reactivity of these chlorides. While derivative *Ia* gave a good yield under conditions reported in literature (benzene, 4 h-reflux), the other derivatives yielded nonuniform products. The reaction was accompanied by formation of a noncyclic product, which in the case of derivatives *Ic* and *Ie* was isolated and identified. Satisfactory yields (Table I) were obtained under modified reaction conditions (toluene, 6 h-reflux). 6-Nitro-2-phenylbenzothiazole derivatives were obtained by direct nitration with nitric sulphuric acid<sup>12-14</sup> (Table II) at a temperature not exceeding 75°C. At the higher temperature the nitration produces the greater amount of dinitro-substituted derivatives. The position of the second nitro group was not determined; reasoning by analogy with 6-nitro-2-phenylbenzothiazole<sup>12</sup>, the nitro group may be in positions 5 and 7. The nitro-derivative was freed of the dinitro-substituted compound by crystallisation from glacial acetic acid in which the latter substance is insoluble<sup>13,14</sup>. The nitro derivatives were reduced by tin powder



In formulae I–IV: *a*, X = H; *b*, X = CH<sub>3</sub>; *c*, X = CH<sub>3</sub>O; *d*, X = Cl, *e*, X = Br, *f*, X = I, *g*, X = NO<sub>2</sub>; *h*, X = 3-NO<sub>2</sub>; where for III*g,h*, X = NH<sub>2</sub>; IV*g,h*, X = NCS.

SCHEME 1

in dilute hydrochloric acid<sup>15,16</sup>. Different yields are due to poor solubility of the tin(IV) complex of the formed amino derivatives in a sodium hydroxide solution which was used to release the amines (Table II). Attempted partial reduction of derivatives II*g* and III*h* by ammonium sulphide has failed, and the product obtained was identical with the fully reduced substances III*g* and III*h*, respectively. Substituted 2-phenyl-6-benzothiazolyl isothiocyanates were prepared by thiophosgene method<sup>17</sup>. Relatively low yields (Table II) are caused both by sparse solubility of the intermediate and final products, and by their difficult isolation and purification.

The infrared spectra of the benzothiazoles (Table III) show characteristic bands in the 1600–1380 cm<sup>-1</sup> region<sup>18–20</sup>. Due to conjugation in the benzothiazole aromatic

TABLE I  
Physical Constants of 2-(4'-X-Phenyl)benzothiazoles

Compd.	X	Yield, %	M.p., °C	M.p., °C, lit.
<i>Ia</i>	H	72	110–113	114 <sup>a</sup>
<i>Ib</i>	CH <sub>3</sub>	94	81–83	85 <sup>b</sup>
<i>Ic</i>	CH <sub>3</sub> O	52	116–118	118–119 <sup>c</sup>
<i>Id</i>	Cl	62	117–120	120–121 <sup>d</sup>
<i>Ie</i>	Br	63	130–132	132–133 <sup>d</sup>
<i>If</i>	I	58	138–142	157–158 <sup>d</sup>
<i>Ig</i>	NO <sub>2</sub>	61	230	231 <sup>c</sup> , 233 <sup>a</sup>
<i>Ih</i>	3-NO <sub>2</sub>	55	184	184 <sup>c</sup>

<sup>a</sup> Ref. 16, <sup>b</sup> ref. 13, <sup>c</sup> ref. 28, <sup>d</sup> ref. 29.

TABLE II  
Properties of 2,6-Disubstituted Benzothiazoles II–IV

Compd. X	Formula (m.w.)	M.p., °C (yield, %)	Calculated/Found	
			% N	% S
2-(4'-X-phenyl)-6-nitrobenzothiazoles				
<i>Ila</i> H	C <sub>13</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub> S (256·3)	187–188 (63)	10·69 10·58	12·50 12·44
<i>Ilb</i> CH <sub>3</sub>	C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> S (270·3)	204–205 (35)	10·36 10·22	11·86 11·81
<i>Ilc</i> CH <sub>3</sub> O	C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> S (286·3)	188–190 (56)	9·78 9·62	11·19 11·27
<i>Ild</i> Cl	C <sub>13</sub> H <sub>7</sub> ClN <sub>2</sub> O <sub>2</sub> S (290·7)	266–267 (62)	9·64 9·18	11·03 11·23
<i>Ile</i> Br	C <sub>13</sub> H <sub>7</sub> BrN <sub>2</sub> O <sub>2</sub> S (355·2)	256–257 (59)	8·36 8·48	9·56 9·31
<i>Ilf</i> I	C <sub>13</sub> H <sub>7</sub> IN <sub>2</sub> O <sub>2</sub> S (382·2)	112–115 (55)	7·33 7·36	8·38 <sup>a</sup>
<i>Ilg</i> NO <sub>2</sub>	C <sub>13</sub> H <sub>7</sub> N <sub>3</sub> O <sub>4</sub> S (301·3)	242–243 (86)	13·96 14·09	10·64 10·54
<i>Ilh</i> 3-NO <sub>2</sub>	C <sub>13</sub> H <sub>7</sub> N <sub>3</sub> O <sub>4</sub> S (301·3)	206 (79)	13·96 14·03	10·64 10·62
2-(4'-X-phenyl)-6-aminobenzothiazoles				
<i>IIIa</i> H	C <sub>13</sub> H <sub>10</sub> N <sub>2</sub> S (226·2)	206 (52)	12·39 12·30	14·19 14·32
<i>IIIb</i> CH <sub>3</sub>	C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> S (240·3)	230–232 (63)	11·52 11·60	13·15 13·02
<i>IIIc</i> CH <sub>3</sub> O	C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> OS (256·3)	162–165 (76)	10·93 10·96	12·52 12·31
<i>IIId</i> Cl	C <sub>13</sub> H <sub>9</sub> ClN <sub>2</sub> S (260·1)	249–251 (31)	10·77 11·02	12·32 12·13
<i>IIIe</i> Br	C <sub>13</sub> H <sub>9</sub> BrN <sub>2</sub> S (305·2)	246–248 (80)	9·18 9·11	10·51 10·59
<i>IIIf</i> I	C <sub>13</sub> H <sub>9</sub> IN <sub>2</sub> S (352·2)	256 <sup>b</sup> (30)	7·96 7·82	9·10 <sup>c</sup>
<i>IIIg</i> NH <sub>2</sub>	C <sub>13</sub> H <sub>11</sub> N <sub>3</sub> S (241·3)	236–242 (65)	17·42 17·48	13·28 13·15
<i>IIIh</i> 3-NH <sub>2</sub>	C <sub>13</sub> H <sub>11</sub> N <sub>2</sub> S (241·3)	178–182 (48)	17·42 17·09	13·28 13·32

TABLE II  
(continued)

Compd. X	Formula (m.w.)	M.p., °C (yield, %)	Calculated/Found	
			% N	% S
2-(4'-X-phenyl)-6-benzothiazolyl isothiocyanates				
<i>IVa</i>	C <sub>14</sub> H <sub>8</sub> N <sub>2</sub> S <sub>2</sub>	149–151	10.46	23.93
H	(268.4)	(52)	10.38	24.01
<i>IVb</i>	C <sub>15</sub> H <sub>10</sub> N <sub>2</sub> S <sub>2</sub>	163–165	9.88	22.62
CH <sub>3</sub>	(282.4)	(61)	10.33	22.99
<i>IVc</i>	C <sub>15</sub> H <sub>10</sub> N <sub>2</sub> OS	215–216	9.39	21.49
CH <sub>3</sub> O	(298.4)	(39)	9.20	21.56
<i>IVd</i>	C <sub>14</sub> H <sub>7</sub> ClN <sub>2</sub> S <sub>2</sub>	162–164	9.25	21.18
Cl	(302.8)	(34)	9.52	21.29
<i>IVe</i>	C <sub>14</sub> H <sub>7</sub> BrN <sub>2</sub> S <sub>2</sub>	183–185	8.08	18.47
Br	(347.3)	(42)	8.15	18.21
<i>IVf</i>	C <sub>14</sub> H <sub>7</sub> IN <sub>2</sub> S <sub>2</sub>	142–144	7.11	16.27
I	(394.3)	(30)	7.24	<sup>d</sup>
<i>IVg</i>	C <sub>15</sub> H <sub>7</sub> N <sub>3</sub> S <sub>3</sub>	216–217	12.90	29.56
NCS	(325.4)	(46)	12.42	29.46
<i>IVh</i>	C <sub>15</sub> H <sub>7</sub> N <sub>3</sub> S <sub>3</sub>	164	12.90	29.56
3-NCS	(325.4)	(53)	12.51	29.86

<sup>a</sup> Calculated: 40.80% C, 1.84% H; found: 40.92% C, 1.89% H; <sup>b</sup> Dec.; <sup>c</sup> Calculated: 44.32% C, 2.60% H; found: 44.03% C, 2.72% H; <sup>d</sup> Calculated: 42.67% C, 1.79% H; found: 42.91% C, 1.81% H.

system, there proceeds an equilibration of the properties of the C=C and C=N bonds and, hence, the reliable assignment of wavenumbers is not possible. The region mentioned above should therefore be regarded as corresponding to skeletal vibrations of the whole benzothiazole system. Complex absorption band in the 2200–2000 cm<sup>-1</sup> region is due to asymmetric vibrations of the NCS group attached to the aromatic ring<sup>21</sup>. The absorption band has three maxima; the position of the first maximum depends on substituents and  $\nu(\text{NCS})_{\text{asym}}$ 's were found to correlate well with Hammett  $\sigma$  substituent constants (Fig. 1). It can be concluded that electron deficiency of the NCS group is affected by substituents in position 4. A relatively high slope (–34.4) of the  $\nu(\text{NCS})_{\text{asym}}$  vs  $\sigma$  plot indicates the less extensive electron shift, compared to 4-substituted phenyl isothiocyanates<sup>21</sup> (–54.8).

The UV spectra of 2-phenyl-6-benzothiazolyl isothiocyanates show absorption

at 220 nm, 250–300 nm, and 300–350 nm (Table IV). While the first two bands do not undergo distinct changes, the last band is sensitive to substituent effects from position 4' of the 2-phenyl ring, and can be assigned to  $\pi\text{-}\pi^*$  electron transitions of the benzilidenimine chromophor<sup>22,23</sup>.

In order to estimate the electronic effect of substituents in position 4' on the reactivity of the NCS group in the 6 position of benzothiazole skeleton, we have studied the kinetics of nucleophilic addition of the  $\text{NH}_2$  group of glycine and of the addition of  $\text{OH}^-$  ions to the NCS group (Table V). Similarly to spectroscopic measurements, also kinetic data, *i.e.* logarithms of the rate constants, were found to correlate well with  $\sigma$  constants (Figs 2 and 3); the reaction constant  $\rho$  for the addition of the  $\text{NH}_2$  group of glycine was 0.51 ( $r = 0.946$ ) and for the addition of  $\text{OH}^-$  ions it was 0.50 ( $r = 0.975$ ). When compared to a series of substituted phenyl isothiocyanates ( $\rho_{\text{NH}_2} = 0.82$ , ref.<sup>24</sup>), in the compounds studied the transmission of the electronic effect of substituent is *c.* 1/3 smaller. From the values of the reaction constants of the addition of both nucleophilic reagents it follows that substituent effects are similar in both cases, although the reaction with  $\text{OH}^-$  ions proceeds at a slower rate. A similar mechanism for both reactions was suggested by Drobnica and Augustin<sup>24,25</sup>. Linear relationship between  $\log k_{\text{NH}_2}$  and  $\log k_{\text{OH}^-}$  was established for parent, unsubstituted isothiocyanates of phenyl, biphenyl, azobenzene, stilbene, diphenyloxide, and 1-naphthyl<sup>26</sup>. The parent compound of this series, IVa, fits well

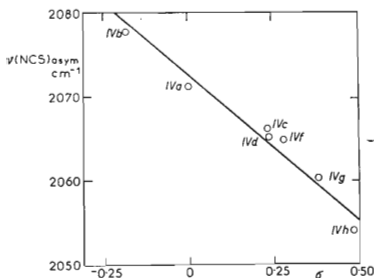


FIG. 1

Plot of Wavenumbers of  $\nu(\text{NCS})_{\text{asym}}$  vs  $\sigma$  for 2-(4'-X-Phenyl)-6-benzothiazolyl Isothiocyanates (Slope  $-34.38$ ;  $r = 0.91$ )

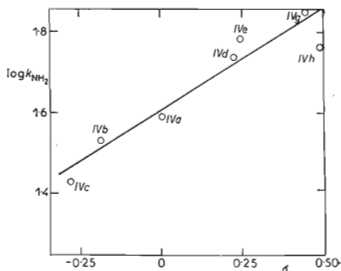


FIG. 2

Dependence of Logarithms of Rate Constants of the Reaction of the NCS Group the  $\text{NH}_2$  Group of Glycine for 2-(4'-X-Phenyl)-6-benzothiazolyl Isothiocyanates ( $\rho = 0.51$ ;  $r = 0.956$ )

this relationship ( $\text{tg } \alpha = 0.78$ ). Derivative *IVh*, with the substituent in position 3', does not differ from a series of 4'-substituted compounds in any of the above considered dependences. It can be then assumed that also in 2-(3'-X-phenyl)-6-benzothiazolyl

TABLE III  
Wavenumbers ( $\text{cm}^{-1}$ ) of Absorption Bands in IR Spectra of 2-(4'-X-Phenyl)-6-benzothiazolyl Isothiocyanates

Compd.	X	$\nu$ of benzothiazole and of phenyl	$\nu(\text{NCS})_{\text{asym}}^a$
<i>IVa</i>	H	1 325, 1 470, 1 505, 1 620	2 071, 2 110, 2 180
<i>IVb</i>	$\text{CH}_3$	1 330, 1 460, 1 505, 1 615	2 078, 2 120, 2 180
<i>IVc</i>	$\text{CH}_3\text{O}$	1 325, 1 360, 1 470, 1 500, 1 575, 1 610	2 040, 2 050, 2 130
<i>IVd</i>	Cl	1 330, 1 430, 1 475, 1 490, 1 610	2 065, 2 140, 2 150
<i>IVe</i>	Br	1 330, 1 420, 1 460, 1 560, 1 620	2 066, 2 140, 2 150
<i>IVf</i>	I	1 330, 1 472, 1 500, 1 590, 1 615	2 065, 2 130, 2 150
<i>IVg</i>	NCS	1 315, 1 460, 1 493, 1 575, 1 610	2 060, 2 110, 2 200
<i>IVh</i>	3-NCS	1 330, 1 470, 1 570, 1 610	2 054, 2 115, 2 150

<sup>a</sup>  $\nu(\text{NCS})_{\text{sym}} 980 \text{ cm}^{-1}$  for all derivatives.

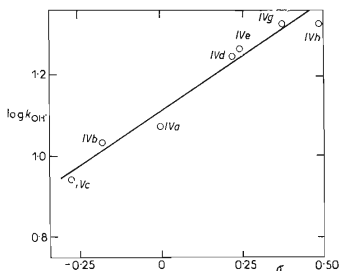


FIG. 3

Dependence of Logarithms of Rate Constants of the Reaction of the NCS Groups of 2-(4'-X-Phenyl)-6-benzothiazolyl Isothiocyanates with  $\text{OH}^-$  Ions ( $\rho = 0.50$ ;  $r = 0.975$ )

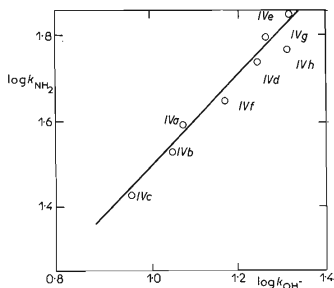


FIG. 4

The  $\log k_{\text{NH}_2}$  vs  $\log k_{\text{OH}^-}$  Plot for 2-(4'-X-Phenyl)-6-benzothiazolyl Isothiocyanates ( $\text{tg } \alpha = -1.10$ ;  $r = 0.97$ )

isothiocyanates the effect of substituents on the NCS group is analogous to their effect in derivatives *IVa-g*. The lower rate constants observed with 2-(4'-iodophenyl)-6-benzothiazolyl isothiocyanate (*IVf*) are likely due to the great size of the molecule. The reactivity decrease is the same for the additions of both nucleophilic reagents (Fig. 4).

TABLE IV

Values of  $\lambda_{\max}$  (nm) and  $\log \epsilon$  in UV Spectra of 2-(4'-X-Phenyl)-6-benzothiazolyl Isothiocyanates

Compd.	X	$\lambda_{\max}$ , nm ( $\log \epsilon$ )			
<i>IVa</i>	H	226 (4.89)	265 (4.43)	287 (4.41)	338 (4.83)
<i>IVb</i>	CH <sub>3</sub>	226 (4.98)	266 (4.53)	288 (4.59)	338 (4.92)
<i>IVc</i>	CH <sub>3</sub> O	224 (4.71)	270 (4.39)	293 (4.45)	329 (4.56)
<i>IVd</i>	Cl	225 (4.67)	268 (4.34)	293 (4.36)	328 (4.49)
<i>IVe</i>	Br	225 (4.72)	268 (4.40)	294 (4.41)	328 (4.55)
<i>IVf</i>	I	225 (5.03)	263 (4.55)	287 (4.60)	324 (4.80)
<i>IVg</i>	NCS	228 (4.70)	268 (4.08)	294 (4.19)	339 (4.75)
<i>IVh</i>	3-NCS	224 (4.83)	263 (4.48)	296 (4.46)	325 (4.64)
<i>Ia</i>	—	220 (4.88)	248 (4.43)	299 (4.72)	308 (4.78)

For purposes of quantitative evaluation of the effect of substituents attached to the 2-position of the phenyl ring on the NCS group in the 6 position of benzothiazole skeleton, the value of transmission coefficient of electronic effect  $\pi'$  (ref.<sup>27</sup>) through benzothiazole ring was calculated. When compared with substituted phenyl isothiocyanates, from the  $\nu(\text{NCS})_{\text{asym}}$  values we obtained  $\pi' = 0.627$ , and from the rate constants of the addition of NH<sub>2</sub> group of glycine,  $\pi' = 0.619$  was calculated. These values indicate the extensive transmission of an electronic effect of the substituent on the NCS group in the studied series of benzothiazolyl isothiocyanates.

## EXPERIMENTAL

### 2-(4'-Substituted phenyl) Benzothiazoles I

To a solution of 31.3 g (0.1 mol) of zinc salt of 2-aminothiophenol in 60 ml of toluene, 0.2 mol of substituted benzoyl chloride were added, and the mixture was refluxed for 6 h. After removal of the solvent by distillation, the base was released by adding 100 ml of 0.5M-NaOH, separated by filtration with suction, and crystallized from 50% aqueous ethanol. The derivatives prepared in such a way are listed in Table I.

## 2-(4'-Substituted phenyl)-6-nitrobenzothiazoles II

A total of 21.1 g (0.1 mol) of 2-phenylbenzothiazole was added with stirring to nitric sulphuric acid (15 g  $\text{NaNO}_3$  in 75 ml conc.  $\text{H}_2\text{SO}_4$ ), such that the temperature did not raise over  $75^\circ\text{C}$ . After the addition was complete, the mixture was stirred for another 1 h, cooled and poured onto an excess of ice. The precipitate was crystallized from glacial acetic acid. The other derivatives, listed in Table II, were prepared similarly.

TABLE V

Rate Constants ( $1 \text{ mol}^{-1} \text{ min}^{-1}$ ) of Reactions of the NCS Group of 2-(4'-X-Phenyl)-6-benzothiazolyl Isothiocyanates with the  $\text{NH}_2$  Group of Glycine ( $k_{\text{NH}_2}$ ) and with  $\text{OH}^-$  Ions ( $k_{\text{OH}^-}$ )

Compd.	X	$k_{\text{NH}_2}$	$k_{\text{OH}^-}$
<i>IVa</i>	H	$39.34 \pm 0.78$	$11.74 \pm 0.52$
<i>IVb</i>	$\text{CH}_3$	$34.18 \pm 0.66$	$11.08 \pm 0.63$
<i>IVc</i>	$\text{CH}_3\text{O}$	$27.24 \pm 0.77$	$8.92 \pm 0.30$
<i>IVd</i>	Cl	$55.00 \pm 0.41$	$17.35 \pm 0.68$
<i>IVe</i>	Br	$61.40 \pm 0.07$	$18.51 \pm 0.54$
<i>IVf</i>	I	$44.66 \pm 0.35$	$14.68 \pm 0.32$
<i>IVg</i>	NCS	$70.82 \pm 0.49$	$20.80 \pm 0.69$
<i>IVh</i>	3-NCS	$57.91 \pm 0.52$	$20.83 \pm 0.81$

## 2-(4'-Substituted phenyl)-6-aminobenzothiazoles III

A mixture of 2.56 g (0.01 mol) of 2-phenyl-6-nitrobenzothiazole, 5 ml of conc. HCl, 95 ml of water, and 11.8 g (0.01 mol) of tin powder was heated for 4 h, while stirring. Then the mixture was filtered while hot and after cooling it was poured into 500–800 ml of 4M-NaOH. The precipitate of 2-phenyl-6-aminobenzothiazole was recrystallized from 50% ethanol. The same procedure was used to prepare derivatives *IIIb*–*IIIh*, Table II.

## 2-(4'-Substituted phenyl)-6-benzothiazolyl Isothiocyanates IV

Saturated solution of 22.6 g (0.1 mol) of 2-phenyl-6-aminobenzothiazole in chloroform was added dropwise to an emulsion of 120 ml of chloroform, 40 ml of dichloroethane, 200 ml of water, and 8 ml (0.11 mol) of freshly distilled thiophosgene. During the addition the mixture was made neutral by adding  $\text{CaCO}_3$ . After the addition of the amino derivative was complete, the mixture was allowed stir for another 3 h. A crude product, isolated from the organic layer, was dissolved in benzene and repeatedly passed through a column filled with  $\text{Al}_2\text{O}_3$ . Then, the benzene solution was partially concentrated and petroleum ether was dropwise added until the liquid has turned turbid. The product was then allowed to crystallize. Prepared benzothiazolyl isothiocyanates are summarized in Table II.



## Spectroscopic Measurements

The infrared spectra were recorded with a double-beam Zeiss, UR-20, spectrophotometer in the 3600—800  $\text{cm}^{-1}$  region. The measurements were carried out with  $2.5 \cdot 10^{-2}$  M chloroform solutions using NaCl cells thick 0.416 mm. The instrument was calibrated with polystyrene film.

The ultraviolet spectra were taken on Specord UV VIS (Zeiss) spectrophotometer in the 215—400 nm region; conc.  $(1.5-5) \cdot 10^{-5}$  M in dioxane, quartz cell thick 10 mm, temperature  $25 \pm 0.2^\circ\text{C}$ .

## Kinetic Measurements

Kinetics of the reactions of isothiocyanates with the  $\text{NH}_2$  group of glycine and with  $\text{OH}^-$  ions was studied spectrophotometrically at  $25 \pm 0.2^\circ\text{C}$  with the aid of Specord UV VIS (Zeiss) instrument and under the conditions of pseudo-monomolecular reaction<sup>24-26</sup>. The pH values of the buffer and the reaction mixture were measured on a pH-meter (Radelkis) equipped with glass and calomel electrodes. The purity of isothiocyanates was checked by thin layer chromatography prior to using in kinetic measurements. The course of the reaction with glycine was followed in a mixture of 10 ml of methanol, 7.8 ml of 0.1 M borate buffer of pH 9.8, and 2 ml of  $5 \cdot 10^{-2}$  M aqueous solution of glycine. The mixture for the reaction of isothiocyanates with  $\text{OH}^-$  ions consisted of 10 ml of methanol and 9.8 ml of 0.1—0.4 M NaOH. Methanolic solution of isothiocyanate (0.2 ml) was added to the reaction mixture maintained at a constant temperature, the initial concentration of the isothiocyanate in the mixture being  $1-5 \cdot 10^{-5}$  M. Apparent rate constants were obtained from the plot of logarithms of extinction changes vs time, the true rate constants were calculated from the apparent ones by dividing the latter by concentration of the reaction component used in excess.

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